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ABSTRACT

The relationship between fall and spring lake chemistry was investigated for five chemical variables of 103 lakes in seven regions of the United States. Strong linear relationships were found between preceding spring and fall values for acid neutralizing capacity (ANC), pH, sulfate, and calcium. These relationships indicate that sampling a large number of lakes during fall overturn, combined with intensive sampling of representative lakes throughout the year, may be a feasible method of estimating changes in chemistry across a geographic region.

INTRODUCTION

Acidic deposition occurs as a regional rather than a point source phenomenon. For policy development, assessment of the number of lakes or "resources at risk" within a region is desirable. However, it is often not possible to sample all the lakes likely to respond to acidic deposition, let alone monitor their chemistry intensively for a long time period. Monitoring a representative (1) set of lakes in a region is one way of addressing this problem. This paper presents evidence that sampling lakes once during the fall turnover period provides an indication of spring lake chemistry. This finding supports the fall index concept used in the Eastern Lakes Survey (2, 3) and may also be applied to the design of a monitoring program.

The Eastern Lake Survey (2, 3) conducted an extensive regional survey of potentially sensitive lakes in the Eastern United States. Single samples were taken from 1800 lakes during the fall overturn period. Fall was chosen as a time of year with low among-lake variability, and low within-lake variability due to the mixing period. This sample was considered an index of annual lake chemistry, and was used to describe regional lake characteristics and to estimate the number of acidic lakes in each region.

The existence of strong spring to fall chemical relationships provides a basis for evaluating and developing a tiered regional monitoring program. Herein we present data to show that seasonal samples from a representative subset of lakes within a region can be used to develop predictive models. Spring data can then be estimated for the larger set of lakes by employing the model with data from single fall samples. The advantages of this type of design over more conventional monitoring efforts are that a greater number of lakes may be sampled across the region, increasing the confidence of regional trend assessments, while keeping sampling costs down.

METHODS

Data used for this analysis were obtained as part of the U.S. Environmental Protection Agency's (EPA) Long-Term Monitoring Project 4). During this project, 103 lakes were monitored at least three times per year, in the spring, summer and fall. Lakes were chosen by individual cooperators in seven regions: Maine (ME); Vermont (VT); the Adirondack region of New York (NY); Minnesota (MN); Michigan (MI); Wisconsin (WI); and the mountainous Southern Blue Ridge region of North Carolina, Georgia and Tennessee (SBR). State abbreviations have been used to identify these regions.

Lakes with low ANC values (< 200 eq L^{-1}) were chosen as potentially sensitive to acidification. No other attempt was made to select lakes which were representative of other lakes within each region. A detailed discussion of how these lakes compare to the population of lakes sampled in the Eastern Lakes Survey is included in (4). Lakes sampled in Vermont, New York, Minnesota, Wisconsin, and the Southern Blue Ridge were similar to lakes in the same regions described by the Eastern Lake Survey. Maine lakes however, were close to the coast, and demonstrated a high sea-salt influence. Lakes sampled on the Upper Peninsula of Michigan were not dominated by Ca as were many of the lakes in that region.

Monitoring of some lakes was initiated as early as 1979, and continued through 1985. Spring samples were taken as soon after ice-out as possible; fall samples were taken during the fall mixing period. Both spring and fall data were not available for all years; however two to four years of data were available for each region. The number of lakes and ranges of variables in each region are shown in Table 1.

Samples were taken 0.5 m below the surface near the deepest part of each lake. ANC was measured by Gran titration (5); SO_4^{-2} by ion chromatography; and Ca by atomic absortion spectrophotometry. Although methodology varied slightly among regions, they remained the same within a region. Further details of sampling, chemical analyses, and quality assurance of the data can be found in (4).

Relationships were characterized by regressing spring values against fall values. Although fall data have associated measurement errors, these errors were small in comparison to the range of fall values. Accordingly, errors about the fall values were ignored, and standard regression was preformed (6).

To test whether slopes and intercepts of these relationships differed among regions, data from all regions were combined, and spring data were regressed on the fall values with the addition of region as indicator variables (7). This exercise showed that relationships differed among regions. These results were consistent with the Eastern Lake Survey (2, 3) which demonstrated many chemical and physical differences among lakes in the same regions. Therefore subsequent analyses were conducted separately for each region.

RESULTS AND DISCUSSION

Results of spring values regressed against the following fall values are shown in Table 2. Included in this table are regression equations, and 95 per cent upper and lower prediction intervals about the lower end of the regression. Confidence bounds increase near the extremes of the data (7), so the larger bounds are presented here to demonstrate how large the prediction interval can be.

The prediction intervals shown in Table 2 demonstrate the range in which the prediction at the lower bound of the regression has a 95% chance of occurring. Figure 1 shows spring ANC plotted against fall ANC for Vermont, with dashed lines representing the 95% prediction intervals. These intervals are relatively wide, demonstrating a moderate variability about the regression line. It may be possible to explain more variation in the data by describing regressions for each year, or by

blocking lakes according to hydraulic residence times or other physical characteristics. Preliminary examination of the data suggests that year is an important covariate in some regions. Assessment of physical attributes was not attempted here, as too few lakes of each type were sampled in each region.

No statistically significant relationship was demonstrated for pH in the Southern Blue Ridge (SBR) region. The range of pH values in this region was small, 5.6 to 7.4, with all but two values in the range of 6.1 to 7.0. This restricted range may explain why no relationship was observed. However, the range of pH values in Minnesota (MN) was equally small, yet a significant relationship was observed. Further examination revealed hydraulic residence times of the SBR reservoirs however were much shorter, ranging from 0.02 to 0.97 years (mean = 0.38 years); those in MN ranged from 1.04 to 7.34 years (mean = 2.68). Such short residence times in the SBR might be expected to have a strong influence on the relationships of seasonal chemistries, although strong relationships were apparent for the remaining variables.

Strong spring to fall relationships were demonstrated for ANC, pH, SO_4^{-2} and Ca in low ANC systems across several regions of the U.S. These relationships may differ annually, and with physical characteristics of the lakes sampled; further investigation of these effects is recommended prior to developing predictive models. Should this relationship be adopted for use in a tiered monitoring program, the subset lakes chosen for seasonal sampling should represent the larger sample, and should encompass the ranges of physical and chemical parameters of interest.

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TABLE 1. The Number of Lakes and Parameter Ranges in Each Region

	Number of Lakes	Range of ANC $\mu eq\ L^{-1}$	Range of pH	Range of SO_4^{-2} $\mu eq\ L^{-1}$	Range of Ca $\mu eq\ L^{-1}$	Range of Organics[1]	Years Included
ME	6	-40 - 60	4.5-6.7	55-100	25 - 80	ND	84-85
VT	36	-30 - 160	4.0-7.4	60-160	40 - 200	1-110 PCU	81-84
NY	17	-60 - 250	4.2-7.0	55-180	20 - 230	1-15 mg L^{-1}	82-85
MN	5	60 - 350	6.0-7.0	30-100	60 - 180	ND	79, 82, 84, 85
MI	12	-50 - 250	4.4-7.0	45-160	20 - 50	ND	82, 84, 85
WI	11	-20 - 50	4.7-6.7	45-160	20 - 85	ND	82, 84, 85
SBR	11	10 - 220	5.6-7.4	10- 65	15 - 140	3-75 PCU	84-85

[1]ND = No data available; PCU = color in platinum-cobalt units; mg L^{-1} = units of DOC.

TABLE 2. Regression Results for Spring Against the Following Fall Chemistry.

	ANC μeq L^{-1}			
	y = m x +b	n	R^2	ANC ± 95% P. I.[1]
ME	y = 0.83 x -2.639	12	0.96	2.4 ± 12.0
VT	y = 0.80 x -3.79	91	0.83	-27.7 ± 32.2
NY	y = 0.79 x +5.90	66	0.80	-41.4 ± 51.6
MN	y = 0.75 x +23.5	15	0.88	73.5 ± 46.7
MI	y = 0.72 x +5.4	32	0.74	-28.4 ± 85.4
WI	y = 0.93 x +10.86	27	0.44	-6.2 ± 30.6
SBR	y = 0.56 x +20.4	21	0.64	26.1 ± 48.2
	pH			
	y = m x +b	n	R^2	pH ± 95% P. I.[1]
ME	y = 0.96 x +0.14	12	0.92	4.47 ± 0.51
VT	y = 0.88 x +0.51	89	0.76	4.42 ± 0.88
NY	y = .95 x +0.24	64	0.89	4.20 ± 0.59
MN	y = 1.20 x -1.1	17	0.69	6.23 ± 0.45
MI	y = 0.92 x +4.9	36	0.95	4.40 ± 0.54
WI	y = 0.88 x +0.89	29	0.81	5.14 ± 0.45
SBR	y = 0.35 x +4.07	21	0.01	
	SO_4^{-2} μeq L^{-1}			
	y = m x +b	n	R^2	SO_4^{-2} ± 95% P.I.[1]
ME	y = 1.13 x -10.0	11	0.96	52.3 ± 9.7
VT	y = 0.73 x +26.2	87	0.58	77.8 ± 22.8
NY	y = 0.83 x +13.4	66	0.77	59.6 ± 24.7
MN	y = 0.96 x +7.83	17	0.75	38.3 ± 21.8
MI	y = 0.90 x +5.20	36	0.91	47.8 ± 16.8
WI	y = 0.90 x +5.88	26	0.80	47.7 ± 27.8
SBR	y = 0.64 x +12.2	21	0.36	20.2 ± 21.2
	Ca μeq L^{-1}			
	y = m x +b	n	R^2	Ca ± 95% P. I.[1]
ME	y = 0.86 x +5.9	12	0.82	29.5 ± 15.2
VT	y = 0.83 x +10.63	89	0.90	42.8 ± 25.9
NY	y = 0.90 x +5.82	66	0.89	28.0 ± 31.1
MN	y = 0.90 x +33.1	17	0.47	90.7 ± 60.8
MI	y = 1.05 x +15.8	35	0.87	35.7 ± 49.2
WI	y = 1.12 x +13.8	28	0.88	51.9 ± 85.5
SBR	y = 0.66 x +14.1	20	0.74	24.6 ± 29.0

[1]P.I. = Prediction Interval for a single prediction at the lower bound of the regression.

Figure 1. Spring ANC ueq L^{-1} versus Fall ANC ueq L^{-1} for Vermont lakes including four years of data.